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PREPARATION OF RARE EARTH DOPED LASER MATERIALS.(U)

JAN 78 R F BELT, L DRAFALL   N00014-76-C-0770

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This report describes the preparation of specific host materials doped with either Ce^{3+} or Pr^{3+}. The materials were prepared by either a solid phase sintering, crystallization from a high temperature flux, or direct growth by the Czochralski method from a melt. Both the amount of dopant and particularly the valence state of cerium were important variables in attempting to control fluorescence. Samples were prepared for both spectral investigations and possible

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laser schemes in the blue-green region. Growth atmospheres and conditions were adjusted to yield the maximum amount of Ce^{3+} in single crystals. $YAG:Ce^{3+}$ and $YAlO_3:Pr$ were prepared in fabricated forms of disks, rectangular rods or cylindrical rods. These crystals were then examined at other laboratories.

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FOREWORD

This Annual Summary Report describes certain related activities in materials preparation. A portion is directly concerned with specific rare earth doped (Ce^{3+} or Pr^{3+}) polycrystalline or single crystal compounds which may prove to be suitable for possible d-f lasing schemes. Another portion of the effort was directed towards the growth, laser fabrication, and testing of YAG:Ce. The report describes all efforts under Contract No. N00014-76-C-0770 for the period November 1, 1976 to November 1, 1977. The contract work was under the coordination of Dr. Van O. Nicolai of the Office of Naval Research.

All compound preparation, single crystal growth, and laser rod fabrication were performed in the laboratories of Airtron Division of Litton Systems, Inc., 200 E. Hanover Avenue, Morris Plains, New Jersey 07950. Dr. Roger F. Belt was the technical director of the project and Dr. Larry Drafall was the project engineer. Karl Jensen was the senior technician. Steven Turner performed all laser material fabrication and Joseph Latore provided all coated optics. Active testing of laser samples was conducted at Naval Research Laboratory by Dr. Leon Esterowitz or by Prof. William Yen of University of Wisconsin.

The report was prepared by Roger F. Belt and Larry Drafall and released for publication in December, 1977.

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1.0 INTRODUCTION

All of the present solid state crystal lasers are based on trivalent rare earth ions with weak forbidden 4f→4f transitions for optical emission and absorption. In recent years more attention has been given to alternate schemes for laser action which use very intense allowed interconfiguration 4f→5d transitions. These excited $4f^{n-1}$→5d bands for most of the rare earth ions are at energies above 50000 cm^{-1}(6.2 ev). Therefore in some single crystals or glasses the fundamental band absorption of the host may prevent fluorescence from 5d bands. In other cases 5d excitation may be quenched by non-radiative decay to overlapping levels of the ground $4f^n$ configuration. However there are important exceptions. The energy level structure of an ion may be one where there are no 4f levels to quench 5d bands. This occurs in certain ions such as Ce^{3+}, Eu^{2+}, Yb^{2+} and a few ions.

Work in several laboratories has been directed towards examining spectra and designing materials which may give 5d-4f type lasing. This class of laser has several potential advantages. Among these are broad optical pump bands centered in the near uv, possible four level operation at 25°C, band emission in the visible, tunability over several hundred Å, and high quantum efficiency. Such a laser is a solid state analog of a dye laser. By appropriate choices of rare earth ion and host, oscillation wavelengths may be adjusted for specific applications in laser technology.

While the spectra, laser scheme, and possible materials have been studied in some systems, no working laser has been developed yet. The reasons for this are many but a greater understanding of allowed transitions of 4f impurity ion systems in crystalline environments is essential as a start. These studies include the crystal structure of the host, the

effect of different coordination about the impurity ion, and symmetry effects. Some of the rough data can be collected from an examination of polycrystalline material but a single crystal is more helpful. Further simplification of emission and absorption in 5d→4f systems may be obtained by examining a system such as Ce^{3+} in $Y_3Al_5O_{12}$. This system was studied[1] and further hosts were reported later[2]. Some operating principles were determined but even for Ce^{3+} the spectra are not predictable and are very sensitive to structure.

The objects of this program included the preparation of selected polycrystalline hosts doped with ions such as Ce^{3+}, Er^{2+}, or Yb^{2+} which may lead to 5d band fluorescence centered around 4800-5000 Å. Once a satisfactory polycrystalline material is obtained, an effort would be made to get single crystals for testing laser action. Most of the anticipated compounds are oxides, fluorides, or oxyfluorides which can be readily prepared in fairly large polished pieces.

The remaining portion of our research effort was devoted to material fabrication of YAG:Ce^{3+}. This material and its preparation have been studied in the past for possible energy transfer schemes to Nd^{3+} in 4f→4f transitions. However, the present investigation is more concerned with the shape and strength of the 5d upwards reabsorption. The results may explain whether this is a Ce^{3+} ionic phenomena or a host dependent property.

2.0 EXPERIMENTAL

Experimental preparations consisted of polycrystalline ceramic sintered powders, small crystals grown from high temperature fluxes, and single crystals of $Y_3Al_5O_{12}$ or $YAlO_3$. The first of these were prepared from 99.99% oxides, carbonates, or nitrates. The required components were

weighed on a balance, mixed at room temperature, and heated in either a platinum or an iridium crucible. The crucibles were used as a susceptor in an RF coil operated at 450 KHz. The temperature of sintering was checked with an optical pyrometer which was calibrated against pure oxides of known melting points. For many of the preparations a form of atmosphere control was essential. This was achieved by enclosing the crucible, its insulation, and the coil in either a quartz or glass container. Gases of O_2, N_2, Ar, or a N_2-H_2 mixture were passed into the bell jar at the bottom and exhausted at the top. The atmosphere was maintained during the entire sintering cycle. Dopants of selected rare earth elements were added in the form of 99.99% oxides and concentration levels were usually 0.1-0.5 atomic per cent substitutions.

Several growth runs were attempted from high temperature fluxes. In these runs the components were added to a 3 inch diameter X 3 inch high platinum crucible. Either a crimped or welded lid formed the closure. The crucible was placed on an Al_2O_3 pedestal and elevated into the hot zone of a resistively heated Globar-element cylindrical furnace. The furnace was heated at 800-1300°C and then a programmed cooling rate of 5-10°C 1 hr. was maintained until the crucible reached 300-400°C. At the lower temperature the flux was cooled to 25°C, the welded lid removed, and the crystals separated by acid leaching of the flux.

The preparation of large single crystals of $Y_3Al_5O_{12}$ or $YAlO_3$ was performed on production Czochralski-type growth stations. Iridium crucibles of 2-3 inch diameter contained the melt and also served as the susceptor for the 450 KHz RF heating. For the garnet crystals [111] seeds were chosen and for $YAlO_3$ a [010] seed was used. Crucibles were enclosed completely within a controlled atmosphere of either N_2-O_2 for

oxidizing or N_2-H_2 for reducing conditions. The crystals were doped with Ce^{3+} and Pr^{3+} in the range of 0.05-0.50 atomic %. Segregation coefficients for both runs were chosen as about 0.8 for $YAlO_3$ and 0.1 for YAG. A crystal length of 4-6 inches and a diameter of 1 inch was grown to provide a sufficient length for a 50 mm laser rod. Smaller geometrical configurations such as disks, rods, or parallelepipeds could also be fabricated from the same boule.

3.0 RESULTS

The starting point for choosing host materials was based partially on computer calculations of fluorescence branching ratios from ^3Po down for Pr^{3+}. Calculations were performed(3) on about 20 crystals and a priority list of about 7 materials was constructed. These included $LuPO_4$, $GdVO_4$, $LuAsO_4$, $YAlO_3$, $Y_3Al_5O_{12}$, $Ca_5(PO_4)_3F$, and $La_2Be_2O_5$. For the hosts to be doped with Ce^{3+} a priority list was based on the principle that excited state absorption via non allowed transitions will be minimal in a crystal with inversion symmetry. Compounds such as Ba_2GdTaO_6, $NaGdO_2$, YP_3O_9, and $YLiF_4$ were possibilities. With the exception of $YLiF_4$ these compounds have never been grown previously in any size for laser examination. Therefore polycrystalline sintered phases were prepared first to check for the presence of any fluorescence under ultra-violet excitation. If in some cases small crystals could be grown from a high temperature solution, a few runs were made under different conditions of heating or cooling.

3.1 Growth of $YAlO_3$:Pr

One of the first single crystals to be examined with Pr^{3+} doping was $YAlO_3$. This crystal has a distorted perovskite structure in which the coordination of the Y^{3+} is eight near oxygen neighbors similar to garnet.

A basic requirement of the undoped host is that it show no absorption except that due to the proposed dopant. Ideally the host band gap should also be larger than about 45000 cm^{-1} or 5.6 e.v. for Pr^{3+} doping since the 5d level starts approximately there. A crystal of $YAlO_3:Pr^{3+}$ was grown along the b-axis with a dopant level of 0.5%. The crystal was grown in a 1% O_2 atmosphere. Figure 1 is a picture of the crystal. Figure 2 shows the absorption spectra of this crystal and some residual absorption occurs around 0.34 μm. The spectrum of YAG:Ce given in Figure 3 suggested the impurity might be Ce^{3+}. However 99.999% Pr^{3+} was used for the dopant oxide and only a few ppm could have contributed to this absorption. $YAlO_3$ in itself is notorious for the appearance of color centers[(4)] during growth and after pumping or irradiation. Great effort has been taken to control impurity levels and growth atmosphere. The elimination of this absorption has not been too successful until lately as claimed by certain workers[(5)]. We have attempted to grow or anneal in a reducing atmosphere which was suggested early in $YAlO_3$ development. However this did not solve the problem completely as illustrated in Figure 2. A H_2 atmosphere also tends to embrittle the crystal. We feel that small amounts of non transition elements such as Ca, Mg, Si may be contributing to residual absorption via defect chemistry. Very high purity reagents, crucibles, and growth ceramic construction materials can give a significant improvement.

3.2 Growth and Fabrication of $YAG:Ce^{3+}$

As explained briefly in the introduction, part of this report is connected with materials preparation for a study of stimulation of 5d→4f transitions in $YAG:Ce^{3+}$. We will not describe all of the spectrascopic data and results because these are to be contained in a separate report

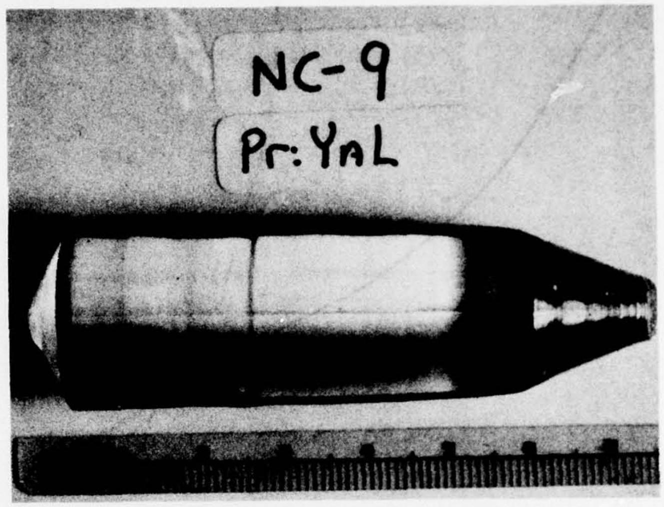


Figure 1. Single crystal of $YAlO_3$:Pr grown along [010].

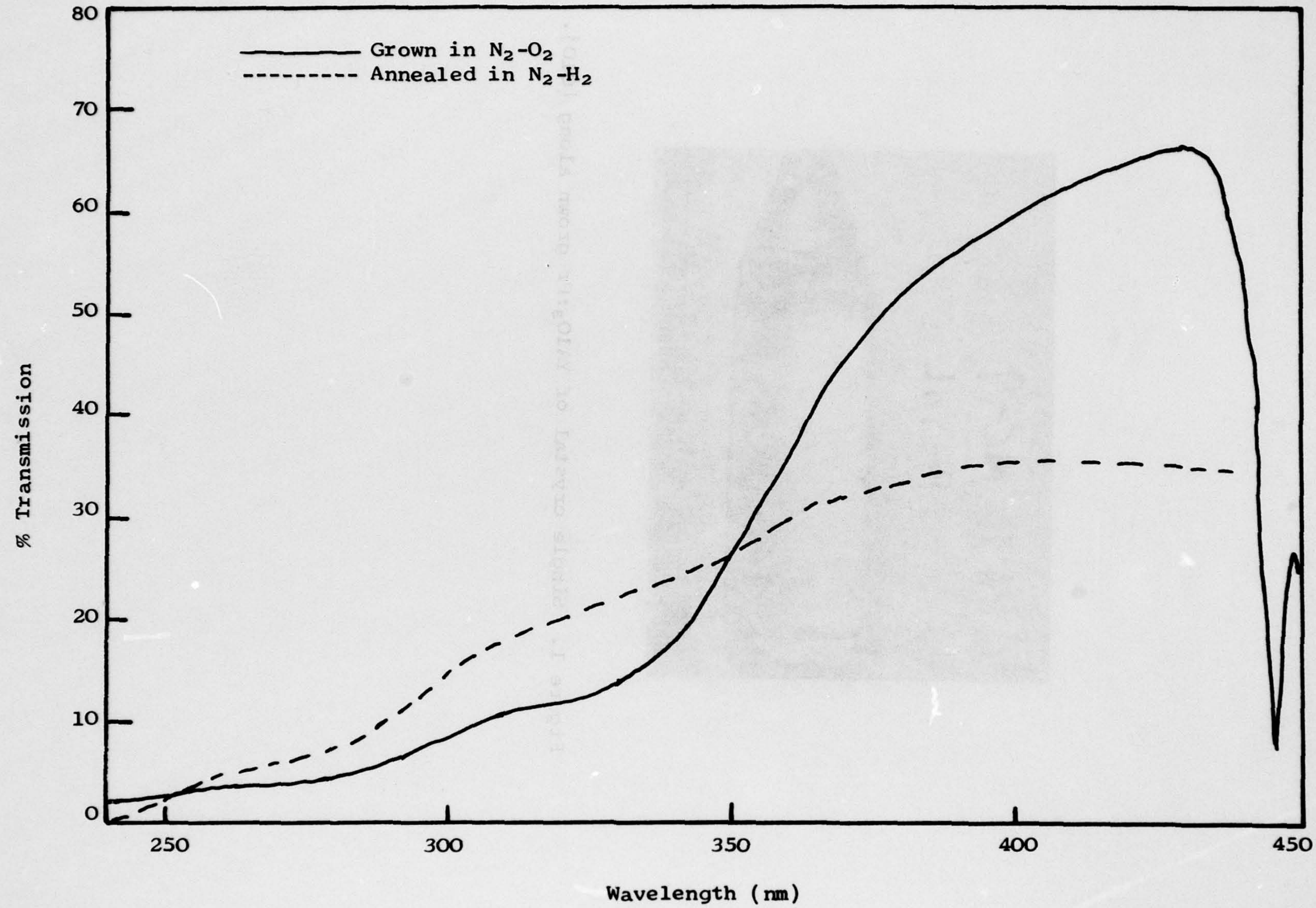


Figure 2. Absorption of $YAlO_3:Pr^{3+}$, b-axis unpolarized.

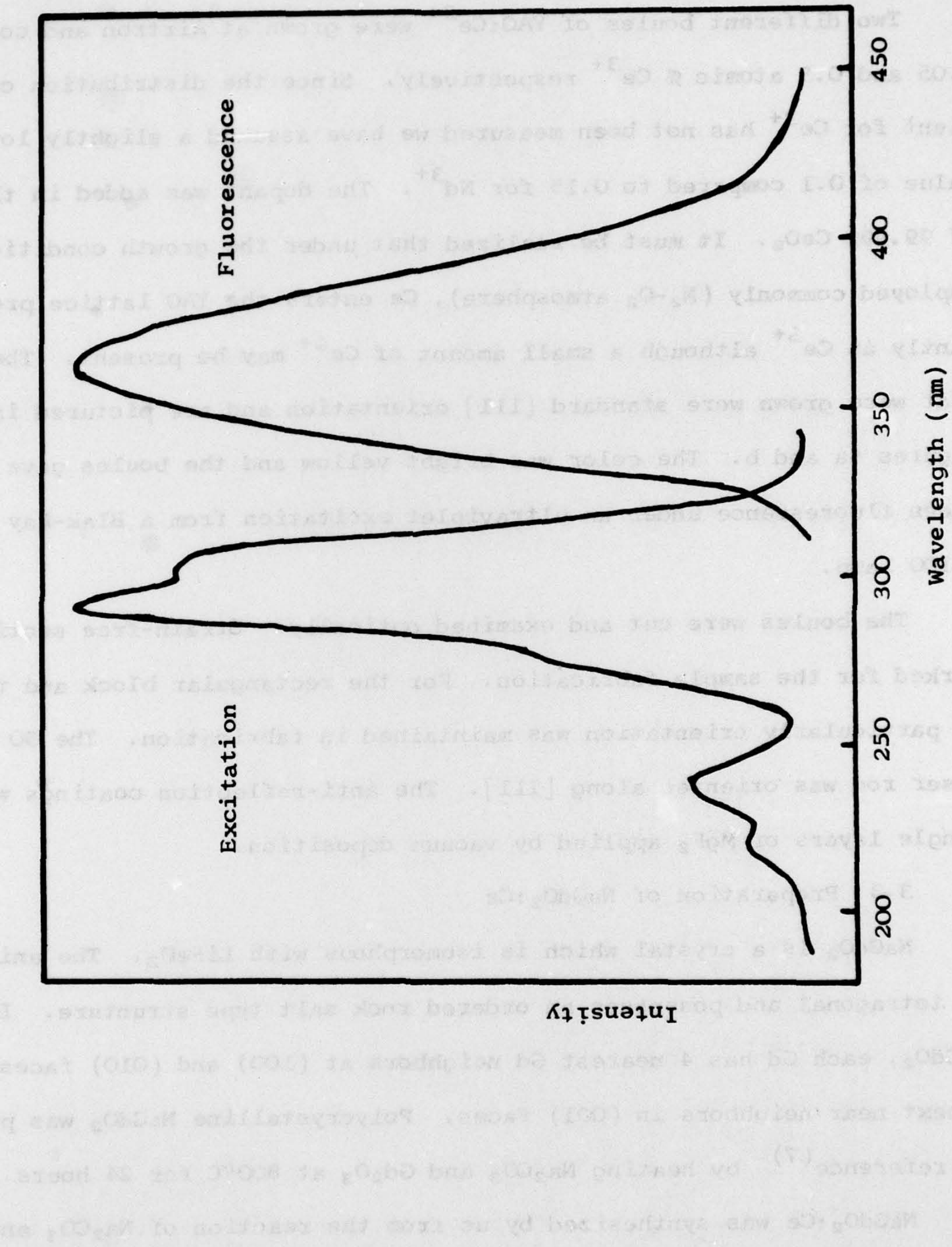


Figure 3. Excitation and Fluorescence of $YAlO_3:Ce^{3+}$

by workers at the University of Wisconsin[6] or elsewhere. The YAG:Ce^{3+} samples we have prepared are listed in Table I. They were chosen for a variety of laser tests.

Two different boules of YAG:Ce^{3+} were grown at Airtron and contained 0.05 and 0.5 atomic % Ce^{3+} respectively. Since the distribution coefficient for Ce^{3+} has not been measured we have assumed a slightly lower value of 0.1 compared to 0.15 for Nd^{3+}. The dopant was added in the form of 99.99% CeO_2. It must be realized that under the growth conditions employed commonly (N_2-O_2 atmosphere), Ce enters the YAG lattice predominantly as Ce^{3+} although a small amount of Ce^{4+} may be present. The boules that were grown were standard [111] orientation and are pictured in Figures 4a and b. The color was bright yellow and the boules gave a yellow-green fluorescence under an ultraviolet excitation from a Blak-Ray Model B-100 lamp.

The boules were cut and examined optically. Strain-free sections were marked for the sample fabrication. For the rectangular block and the disc, no particularly orientation was maintained in fabrication. The 50 mm long laser rod was oriented along [111]. The anti-reflection coatings were single layers of MgF_2 applied by vacuum deposition.

3.3 Preparation of $NaGdO_2$:Ce

$NaGdO_2$ is a crystal which is isomorphous with $LiFeO_2$. The unit cell is tetragonal and possesses an ordered rock salt type structure. In $NaGdO_2$, each Gd has 4 nearest Gd neighbors at (100) and (010) faces and 4 next near neighbors in (001) faces. Polycrystalline $NaGdO_2$ was prepared in reference[7] by heating Na_2CO_3 and Gd_2O_3 at 800°C for 24 hours.

$NaGdO_2$:Ce was synthesized by us from the reaction of Na_2CO_3 and Gd_2O_3 with the doping agent cerium carbonate. The starting chemical of

TABLE I

Polishing and Fabrication Specifications for YAG:Ce

Sample 1

One rectangular block of dimensions 10 x 8 x 5 mm $\pm$ 0.1 mm

10 x 5 faces flat and parallel to laser specs.
10 x 8 faces polished and perpendicular to other faces, also flat
8 x 5 faces polished and perpendicular to other faces and flat

AR coated on 10 x 5 faces for 5000-6000A

Sample 2

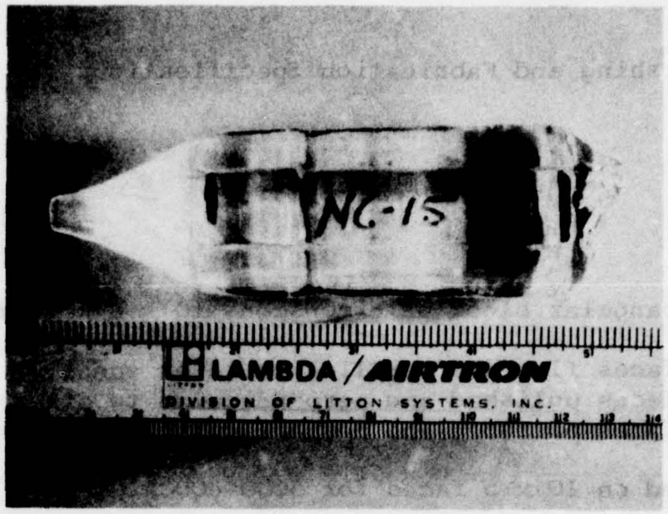
One short rod or disc, 7.00 mm diameter x 5 $\pm$ 0.1 mm long

Ends polished to laser rod specs
AR coated on ends for 5000-6000A

Sample 3

One cylindrical laser rod, 6.95 $\pm$ 0.01 cm diameter x 50^{+1}_{-0} mm long; flat-flat ends polished to $\lambda/10$ flatness, 10 seconds parallelism, and 5 minutes perpendicularity.
AR coated on ends for 5000-6000A

(a)



(b)

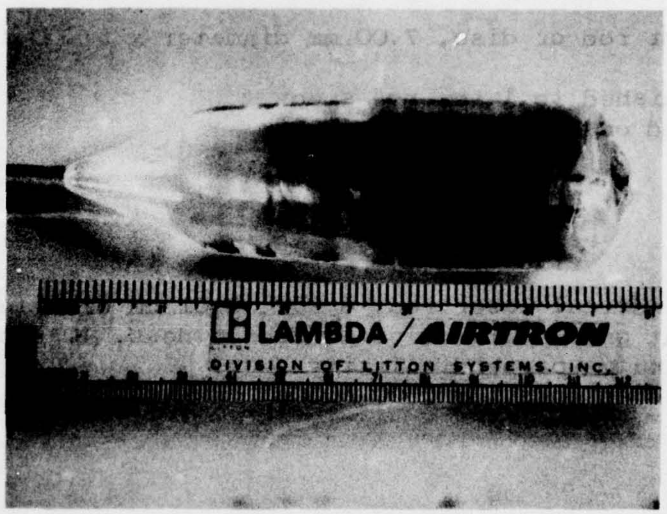


Figure 4. Grown boules of YAG:Ce
(a) 0.05% Ce (b) 0.5% Ce

cerium carbonate according to the analysis had a Ce^{4+} to Ce^{3+} ratio of 2:1. The doping of 0.5 mole % was calculated using this ratio. The mixed powders were pressed isostatically to 30,000 pounds/sq. inch and heated then to 1120°C in air. A portion was also reheated in forming gas which is 85% N_2 and 15% H_2. No X-ray powder diffraction data were available for $NaGdO_2$ but it is isomorphous with tetragonal $LiFeO_2$. The above reaction produced a tetragonal phase which was presumably $NaGdO_2$. At higher temperatures of 1300°C a cubic phase was synthesized which probably corresponds to the cubic disordered modification observed in α-$LiFeO_2$.

3.4 Preparation of Ba_2GdTaO_6:Ce

The fluorescence of Eu^{3+} in mixed metal oxides of the type Ba_2GdNbO_6 was studied[8] in detail. The compound has an ordered perovskite structure with Oh symmetry for the rare earth ion.[9] We have chosen to prepare an isomorphous compound of the same structure. Ba_2GdTaO_6:Ce was prepared by the following reaction: $4BaCO_3 + (1\text{-}x)Gd_2O_3 + xCe(CO_3)_2 + Ta_2O_5 \rightarrow 2Ba_2Gd_{(1-x)}Ce_xTaO_6 + (4+2X)CO_2$ The doping level for Ce was 0.5 mole %. The above chemicals were mixed, pressed into pellets at 30,000 psi, and sintered at 1400°C in air. X-ray diffraction identified well crystallized Ba_2GdTaO_6 with some very minor extraneous peaks. The pellets were reground and heated again to 1400°C in forming gas. This time a complete reaction occurred. The fluorescence was slightly better after the forming gas treatment when samples were checked under ultraviolet excitation.

3.5 Preparation of YP_3O_9:Ce

The structures of the metaphosphates RP_3O_9 (R=rare earth, or Y) again are dependent on the size of the rare earth. Large ions lead to orthorhombic crystals and small ions give monoclinic crystals. The site symmetry in the two structures is different for the rare earth polyhedra.

In NdP_3O_9, the Nd atoms are 8 coordinated with a 2 fold symmetry axis. In YP_3O_9, there are two Y sites, each 6 coordinated but one pair has inversion symmetry and the other does not. Polycrystalline powders of YP_3O_9 were prepared by the reaction of Y_2O_3, $(NH_4)_2HPO_4$, $Ce(CO_3)_2$ with Li_2CO_3 as a flux.[10] The mixture was heated in air to 890°C but could not be identified by x-ray diffraction due to very limited powder x-ray data for YP_3O_9. The material was then heated to 900°C in forming gas where considerable corrosion of the platinum crucible occurred to the extent the vessel had to be scrapped. At high temperatures phosphates are quite reactive with platinum. The compound heated in forming gas also could not be identified but some fluorescence was noted.

Small single crystals of RP_3O_9 type metaphosphates can be prepared by cooling a solution of R_2O_3, P_2O_5, HPO_3 and NaF from 930°C to 870°C.[11] Crystals can be separated by leaching or crystallizing on a platinum wire. We have attempted this technique with cerium doping but no satisfactory results were obtained.

3.6 Preparation of $GdVO_4$:Pr

Single crystals were grown using a mixture of 96 mole % $Pb_2V_2O_7$ flux and 4 mole % Gd_2O_3.[12] The dopant level was 0.5 mole % Pr_6O_{11} with a distribution coefficient of about 0.3. The lead pyrovanadate flux was prepared by heating stoichiometric quantities PbO and V_2O_5. The charged 2" x 2" platinum crucible with lid was "soaked" at 1325°C for several hours and then lowered to 960°C at a rate of about 2°/hr. The furnace was then turned off and cooled to room temperature. The flux was dissolved in a 5:1 dilute HNO_3 solution. Weight loss of the flux during the growth run was 0.5%. Many small bladed crystals of $GdVO_4$:Pr grew throughout the crucible (Figure 5). The largest crystals were approxi-

Figure 5. Flux grown $GdVO_4$:Pr crystals.

Figure 6. Flux grown $LuPO_4$:Pr crystals.

mately 17mm long x 1/2 x 1/2 mm, but most were 3-4 mm long. A bright red fluorescence of the crystals was observed under ultraviolet excitation.

3.7 Preparation of $LuPO_4$:Pr

Single crystals were grown by the flux method. The dopant level of 0.5 mole % Pr^{3+} was used with the distribution coefficient estimated at 0.1 since the ionic radius of Pr^{3+} is much larger than Lu^{3+}. A mixture of 95.1 wt % $Pb_2P_2O_7$ flux and 4.9 wt % Lu_2O_3 with the dopant Pr_6O_{11} was used for the starting charge.(13) The $Pb_2P_2O_7$ flux was prepared by dehydrating $PbHPO_4$ at 1000°C. The charged 2" x 2" Pt crucible with lid was heated and held at 1250°C for 6 hours and then cooled to 925°C at a rate of approximately 1.5°/hr. At 925°C the furnace was turned off and cooled to room temperature. About 20 wt % flux evaporated during the run. A dilute 5:1 solution of HNO_3 was used to dissolve the flux. The crystals grown were light green in color with platy habits. Many crystals had flux inclusions while others were clear. The largest crystal was approximately 7 mm x 4 x 1 mm with numerous smaller ones. A picture of the crystals is given in Figure 6.

3.8 Preparation of ZrO_2:Ce

Towards the end of the present program, oxides with fluorite structure were suggested as possible hosts which may give emission in the green when doped with Ce. During the writing of this report, one experiment was attempted and the results were rather inconclusive. Further experiments are to be conducted where doping levels, phases, different compounds, and mode of preparation can be examined thoroughly.

ZrO_2 is the principal oxide with a fluorite structure. However this structure occurs only in the stabilized form prepared by addition of 5-15 mole % of CaO, MgO, Y_2O_3, or other rare earths. Under these circumstances

the single phase at the melting point and room temperature is cubic. Pure ZrO_2 or with 1.0% Ce doping undergoes destructive phase transitions to monoclinic and tetragonal structures.

At this time we will not go into details on the preparation of large single crystals of stabilized ZrO2. Most phases melt above 2450°C, the melting point of iridium. Thus sintered preparations can be formed in oxidizing atmospheres with iridium crucibles. The main methods for small crystals involve a flux technique or a system where no metal crucible is used. We have prepared some small crystals of stabilized ZrO_2:Ce using RF heating. The stabilizer was Y_2O_3 and the doping level was 0.1% Ce. Under the method of preparation using an oxidizing atmosphere, the valence states of Ce are not known precisely yet. However the crystallites were colored light yellow. There was also some evidence of segregation of Ce since the color was not uniform throughout the melt. Photographs of the crystals are given in Figures 7a and b. Physical data such as absorption spectra were not completed. An examination of the crystals under an ultraviolet lamp did not show any strong fluorescence.

Two additional experiments were attempted with the crystals. Since the preparation was performed in air, pieces of the crystals were placed in an iridium crucible and heated to about 2000°C under N_2-H_2 gas. The crystals were then cooled and examined again for fluorescence. No results were found although the color of the crystals was changed to a lighter yellow. A second experiment involved the x-ray radiation of a crystal. This was done by placing a sample near the port of a copper anode tube operated at 35 KV and 7 ma. No visible changes were noted in the crystal and fluorescence was not observed under ultraviolet excitation.

(a)

(b)

Figure 7. Single crystal pieces of ZrO_2:Ce.

4.0 CONCLUSIONS

Two common and related single crystals doped with Ce were prepared for attempts to get laser action involving 5d → 4f transitions. Both $Y_3Al_5O_{12}$ and $YAlO_3$ were grown in large single crystals Samples doped with Ce^{3+} give fluorescence but residual absorption in the near ultraviolet and the emission wavelength presented problems. In an effort to study the source of the band transitions, shape, and strength of 5d reabsorption a variety of polished YAG:Ce^{3+} samples was prepared and delivered to academic contractors. Two doping levels were chosen.

The examination and preparation of other suitable hosts doped with Ce were continued. While some fluorescence is observed in these compounds, emission at the desired wavelength is difficult to achieve. Furthermore the possibility of growing single crystals was always a consideration. Theoretical data on previously examined structures provided a starting point. The best choice now appears to be oxides with a fluorite structure. Some work on this system has begun.

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